*Macromolecules* **2000,** *33,* 2192−2199

# Effect of Aging and Conditioning on Diffusion and Sorption of Small Molecules in Polymer Glasses

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*Received April 26, 1999; Revised Manuscript Received November 18, 1999*

ABSTRACT: We report measurements on diffusion of $CO_2$ and Ar in aged and conditioned (exposed to high $CO_2$ pressure) samples of BPA-PC. In contrast to intuitive expectations and some previous experimental results on diffusion of larger molecules in polymer glasses, diffusion in a “more open” conditioned matrix is slower than in a denser aged one. We offer an explanation of this effect based on the recently developed site distribution model for sorption and transport of small molecules in polymer glasses. The observed modification of diffusion rates could be described in terms of increasing activation energy for gas diffusion in conditioned in comparison with aged samples. This difference of activation energies could be understood through changes in free volume distribution, which were evaluated from the measured sorption isotherms.

## 1. Introduction

The physical aging and conditioning (exposure to high gas pressures) could influence the solubility and transport of small molecules in polymer glasses.[1,2] The effect of those treatments on gas solubility in polymers is described as follows: The change in sorption parameters is related to the change of free volume due to aging or conditioning. It is generally accepted that aging decreases free volume and, therefore, gas solubility in a polymer matrix, while conditioning “opens” the polymer matrix, increasing its free volume and gas solubility. On the other hand, there is some lack in our understanding of what happens with the diffusivity of small molecules in a glassy matrix during the course of conditioning or aging. The first and very intuitive guess would be that gas transport is easier in a more “open” matrix, and one could expect that conditioning should enhance, while aging slows down diffusivity of small molecules in a polymer. Those changes in diffusivity as a result of polymer pretreatment predicts the “free volume” (FV) theory,[3] and they were observed in some experiments.[4,5] The relevant examples here are the slowing down of methylene diffusion in polystyrene as a result of aging[4] and the similar effect for dye diffusion in various glassy polymers.[5] Also, our experience with nonpolymeric materials suggests that diffusion in “more open” structures is usually much faster. There are numerous data on decreasing of diffusivity and concomitant volume relaxation in metallic glasses.[6] A similar effect was observed also for ion transport in silicate glasses.[7] So, the slowing down of diffusivity as result of volume relaxation in glassy systems appears to be a rather general trend. The FV concept explains this phenomenon through the collective character of transport in glassy systems, where the diffusional step is assisted by a rearrangement of a relatively large number of structural segments. In this situation available free volume becomes a main parameter that controls diffusion.

However, if we deal with the transport of small enough molecules such as light gases in polymers or hydrogen in metals, one could experience a different situation, which resembles interstitial diffusion in crystalline solids. Transport in this case has a relatively low degree of cooperativity, and the diffusional step requires only a moderate displacement of few structural elements of a matrix. Is the effect of changes in glass free volume on the diffusion of these “interstitial“ tracers similar to that for the case of bigger molecules? It is not easy to answer this question. Restricting our consideration to the case of gas diffusion in glassy polymers, one can note that the changes in polymer morphology (and its density) introduced by aging are very small. It is not clear how these small modifications in free volume influence the potential landscape for a diffusant molecule. Moreover, aging or conditioning could affect also the relaxation dynamics of polymer chains. It is rather difficult to treat all the effects mentioned above quantitatively. That is why the intuitive idea that also an interstitial-type diffusion is faster in a more “open” polymer matrix could be, in principle, erroneous. Some experimental evidences of such a case are indeed reported in the literature. Wonders and Paul[8] reported about slowing down $CO_2$ transport in BPA-PC as a result of sample conditioning. The observed increase of the time lags with conditioning pressure measured in permeation experiment was explained in ref 8 within the framework of the dual sorption model. It was proposed that increases in time lags are qualitatively consistent with an increase in Langmuir sorption capacity, caused by polymer dilatation due to $CO_2$ exposure. In a more recent work Jordan et al.[9] present data on $CO_2$ diffusivity in BPA-PC, measured during pressurization and depressurization cycles. For a small pressure limit they found that similar to results of ref 8 diffusion slows down in a conditioned sample. On the contrary, in the high-pressure limit, transport was quicker in conditioned than in the “as-received” sample as it would be expected by FV theory. This change in effect of conditioning on $CO_2$ diffusion in glassy polymer was explained in ref 9 as an interplay of different parameters of the dual sorption model, which could lead to the different change in diffusivities for high- and low-pressure limits. The results of refs 8 and 9 show that increase in free volume of glassy matrix does not always mean enhancement of transport of small penetrants.

10.1021/ma990642a CCC: $19.00

In this work we continue to discuss the influence of variations in free volume on diffusion in glassy polymers. Complementary to refs 8 and 9, we are using both conditioning and aging as a means for free volume modification. We present new experimental data on diffusion of $CO_2$ in aged and conditioned samples of BPA-PC. Similarly to refs 8 and 9 we found that gas diffusion in the "as-received" polymer was faster than in conditioned ones. Aging of the "as-received" sample leads to the additional acceleration of gas transport. The diffusion coefficients were measured as a function of gas concentrations and temperatures. These two sets of data help not only us to discuss modifications in diffusion coefficients and in activation energies of diffusion due to polymer pretreatment but also offer the explanation of experimental data in the framework of the recently developed site distribution model for sorption and transport of small molecules in polymer glasses. We propose that the observed changes in diffusion rates could be described in terms of increasing activation energy for gas diffusion in conditioned compared to aged sample. This difference of activation energies could be understood through the changes in free volume distribution, which were evaluated from the measured sorption and dilatation isotherms. This article is organized in the following way. The next section describes experimental details of this work. Section 3 deals with characterization of changes that occur in the polymer matrix due to pretreatment. In section 4 we present data on diffusion of $CO_2$ in aged and conditioned samples of BPA-PC and offer an interpretation of experimental results. Section 5 contains a discussion of the role of the size of gas molecules in the change of solubility and transport properties of polymer due to pretreatment. Section 6 summarizes our work.

## 2. Experimental Section

**(a) Sample Preparation and Measurements.** BPA-PC was obtained from the Bayer Co. in the form of foil of thickness 0.125 mm. Samples used in solubility, dilatation, and diffusion measurements at $T = 35$ °C were prepared in the following way: Aged samples were prepared by annealing at $T = 135$ °C for 163 h in air. Sample conditioning was performed by exposure of "as-received" sample to $CO_2$ at pressure $p = 15$ bar for 96 h. Samples used in diffusion measurements at different temperatures were aged at $T = 130$ °C for 260 h in air and conditioned in $CO_2$ atmosphere at pressure $p = 30$ bar for 26 h and then at $p = 33$ bar for 22 h.

For the solubility and diffusivity measurements we employed the standard volumetric technique and used the experimental setup described in ref 10. The dilatometer, described in ref 11, was used for the measurements of volume changes of polymer due to gas dissolution. The mechanical spectroscopy was performed using homemade torsional pendulum[12] at frequency $f = 0.73$ Hz.

**(b) Measurements of Diffusion Coefficient.** To compare the gas diffusivities in the different polymer samples, one should select an adequate procedure for it, because the diffusion coefficient $D$ depends strongly on concentration $c$. One possibility would be to compare diffusion coefficients measured for the same concentrations of dissolved gas in the samples. To follow this way, one needs to know accurate pressure−concentration isotherms for each polymer−gas system and each temperature. Such types of measurements were done for diffusion of $CO_2$ at $T = 35$ °C.

For the comparison of diffusion coefficients at different temperatures another procedure that appears through the following rather general consideration was chosen. The reasons for the dependence $D(c)$ are direct or indirect interactions between dissolved gas molecules. For example, the site distribution model[13] explains $D(c)$ through the indirect interactions of gas molecules due to the competitive occupancy of sorption sites, while the dual sorption model[14] assumes competitive occupancy of "normal" and "Langmuir" sites. Particularly those "interactions" that contribute to the dependence of $D$ on $c$ are also responsible for the nonlinear concentration−pressure ($c-p$) isotherms, known for gas sorption in polymer glasses. In the limit of low gas pressure the number of dissolved molecules could be so small that they practically cannot feel the presence of other gas molecules in polymer. This corresponds to an ideal dilute (in the thermodynamic sense) solution, and in this limit $c-p$ isotherms are linear and $c \propto p$ (Henrian regime) and $D(c) =$ const as was documented in ref 15. One can estimate the pressure interval where these relationships are fulfilled by using any predictive model of sorption. For the small pressure limit one can write $c \approx K(T)p + B(T)p^2$, where $K(T)$ and $B(T)$ are model-dependent coefficients. The diffusion coefficient, measured at gas pressures $p \ll K(T)/B(T)$, will be independent of gas pressure and, therefore, concentration. The right choice of experimental pressure interval could be verified by the comparison of $D$ for few values of $p$. The advantage of this way of measuring diffusion coefficients for different polymer samples is that one does not need to know accurate sorption isotherms $c(p,T)$.

## 3. Characterization of Polymer Samples

To get some understanding of how pretreatment alters the diffusivity of small molecules, it is important to quantify changes that occur in the polymer matrix during aging or conditioning. To this end the concentration−pressure and volume−pressure isotherms for sorption of $CO_2$ in aged and conditioned samples of BPA-PC were measured and analyzed with the aid of the site distribution (SD) model. Since the parameters of the SD model are sensitive to the polymer morphology,[16] this analysis provides us with information about the changes in polymer matrix induced by pretreatment. Let us briefly mention some important points of the SD model. For the detailed discussion the reader is referred to the original works (refs 13 and 16).

**3.1. The Site Distribution Model.** In the framework of gas sorption phenomena the nonequilibrium structure of a polymer matrix could be characterized through the distribution of volumes $n(V_h)$ of the sorption sites. The sorption sites or holes correspond to the local minima of the Gibbs free energy of gas molecule in a polymer. The volume distribution appears because the volume fluctuations of polymer liquid are frozen in due to quenching below the glass transition temperature $T_g$ and could be expressed according to Bueche[17] as

$$n(V_h) = \frac{1}{\sigma_V\sqrt{\pi}} \exp\left(-\frac{(V_h - V_h^0)^2}{{\sigma_V}^2}\right) \qquad (1)$$

where $\sigma_V = (2k_BT_gV_h^0/B)^{1/2}$ is the width of the distribution, $V_h^0$ is its average value, and $B$ is the bulk modulus of the polymer in the liquid state at the glass transition temperature $T_g$. The parameters of the free volume distribution could be calculated from dilatometric data as discussed in ref 16.

The occupation of the hole of the volume $V_h$ by the gas molecule of the volume $V_g > V_h$ causes elastic distortion of the polymer matrix and leads to the elastic contribution $G_{el}$ in the sorption energy $G$:

$$G = G_r + G_{el} \qquad (2)$$

The remaining part $G_r$ contains the contributions from the van der Waals interactions between the polymer

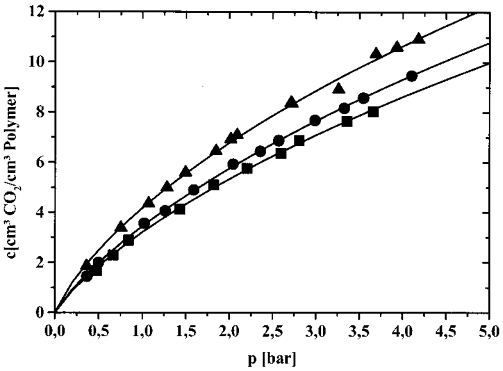

**Figure 1.** Experimental pressure−concentration isotherms for $CO_2$ in the aged (squares), as-received (circles), and conditioned (triangles) samples of BPA-PC at $T = 35$ °C. The solid lines are calculated using the SD model (eq A1) with parameters $G^0 = 18.5$ kJ/mol, $\sigma_G = 9.7$ kJ/mol for aged, $G^0 = 18.0$ kJ/mol, $\sigma_G = 9.4$ kJ/mol for as-received, and $G^0 = 18.1$ kJ/mol, $\sigma_G = 10.0$ kJ/mol for conditioned samples.

**Table 1. Parameters of Energy and Volume Distributions for As-Received, Aged, and Conditioned Samples, Calculated from Experimental Sorption (Figure 1) and Dilatation (Ref 18) Isotherms**

| | $G^0$, kJ/mol | $\sigma_G$, kJ/mol | $V_h^0$, cm$^3$/mol | $\sigma_V$, cm$^3$/mol |
|---|---|---|---|---|
| as-received | 18.0 | 9.4 | 17.4 | 3.9 |
| aged | 18.5 | 9.7 | 16.9 | 3.9 |
| conditioned | 18.1 | 10.0 | 17.5 | 4.1 |
| aged/conditioned | 1.02 | 0.97 | 0.97 | 0.95 |

segments and gas molecules as well as the change in entropy of the dissolved gas molecule in comparison with the reference gas state. While the elastic contribution in the sorption energy $G_{el}$ depends on the hole size and could vary with the site volume $V_h$, the rest energy $G_r$ is assumed to be the same for all sorption sites and, therefore, cold not be changed during a polymer pretreatment. Clearly, the volume distribution $n(V_h)$ leads to the distribution of the sorption site energies $n(G)$. One can show[13] that this distribution is also Gaussian

$$n(G) = \frac{1}{\sigma_G\sqrt{\pi}} \exp\left(-\frac{(G - G^0)^2}{{\sigma_G}^2}\right) \tag{3}$$

and parameters of this distribution $G^0$ and $\sigma_G$ could be determined from sorption isotherms.

**3.2. Characterization of the Aged and Conditioned Samples.** The experimental concentration−pressure ($c$−$p$) isotherms are presented in Figure 1. The solubility of $CO_2$ is larger in conditioned samples then in aged ones. To get information about the change in free volume distributions caused by pretreatment, we also measured polymer dilatation during gas sorption (volume−pressure isotherms).[22] The parameters of volume and energy distributions evaluated within the SD model from these isotherms are summarized in Table 1.

In the following discussion we concentrate only on the difference between the parameters of aged and conditioned samples because of two reasons. First, "as-received" samples have a less defined history, and therefore they could not serve as a proper reference for comparison with the state after pretreatment. Second, because the changes in parameters of the volume and energy distributions are small, it is more meaningful to consider aged and conditioned states only, where these differences are larger. As one can see from Table 1, pretreatment influences both mean hole volume/mean hole energy and widths of their distributions. Conditioned samples have a wider distribution of hole volumes $\sigma_V$ and a larger value of $V_h^0$ than the aged sample. As a result of these changes in volume distribution, the average sorption energy $G^0$ is smaller and $\sigma_G$ is larger in conditioned sample in comparison with the aged one.

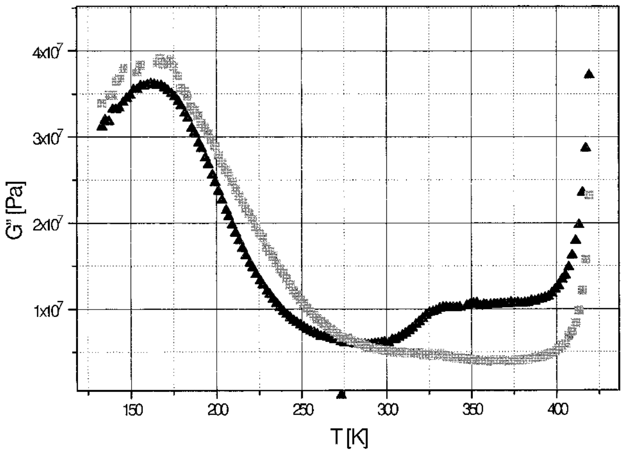

**Figure 2.** Relaxation spectra (loss modulus $G''$ as a function of temperature $T$) for the aged (squares) and conditioned (triangles) samples of PBA-PC measured with the torsional pendulum at frequency $f = 0.73$ Hz.

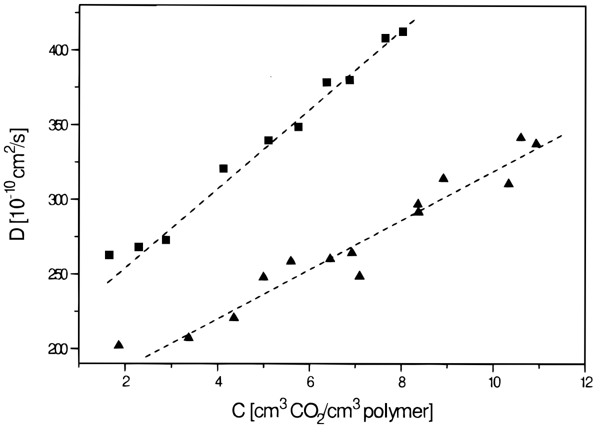

**Figure 3.** Concentration dependence of diffusion coefficient of $CO_2$ in aged (squares) and conditioned (triangles) samples of BPA-PC at $T = 35$ °C evaluated from the sorption kinetics. Lines are drawn to guide the eye.

To characterize changes in dynamics of polymer chains due to pretreatment, mechanical relaxation spectra of aged and conditioned samples were measured with the torsional pendulum at the frequency of 0.73 Hz (Figure 2). One can see that in the aged sample the $\beta$-relaxation is suppressed and the $\gamma$-peak is slightly moved toward higher temperatures (higher activation energies). The intensity of the $\gamma$-peak is larger for the aged sample, which could be attributed to the enhancement of relaxation strength for the side groups participating in this $\gamma$-process.

## 4. Effect of Pretreatment on Diffusion of Gas Molecules

The measured values of the diffusion coefficient of $CO_2$ in aged and in conditioned samples are presented in Figures 3 and 4. Diffusion in the conditioned sample was slower than in the aged one for the range of

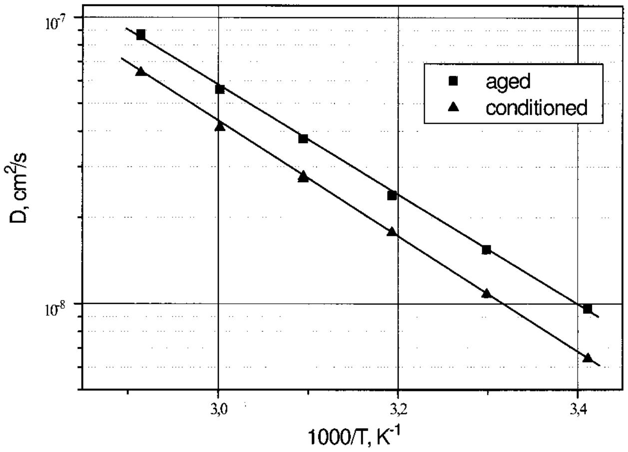

**Figure 4.** Temperature dependence of diffusion coefficient of $CO_2$ in aged (squares) and conditioned (triangles) samples of BPA-PC measured at the dilute solution limit. Solid lines corresponds to Arrhenius fit with $D_0 = 0.035$ cm$^2$/s and $Q = 36.9$ kJ/mol for aged and $D_0 = 0.039$ cm$^2$/s and $Q = 38.0$ kJ/mol for conditioned samples.

concentrations (Figure 3) and temperatures (Figure 4). Additional experiments with Ar demonstrated a similar behavior. The ratio of $D_{\mathrm{aged}}/D_{\mathrm{cond}}$ is about 1.4 in the interval of concentrations and temperatures covered in this study. The values for $CO_2$ diffusion coefficient in the “as-received” sample (not shown in Figure 3) are lower than for aged sample but higher than in conditioned ones. This means that $D_{\mathrm{aged}} > D_{\mathrm{as-received}} > D_{\mathrm{cond}}$ while free volume fraction (FVF) follows the relation $\mathrm{FVF}_{\mathrm{aged}} < \mathrm{FVF}_{\mathrm{as-received}} < \mathrm{FVF}_{\mathrm{cond}}$. This result contradicts the predictions of FV theory[3] where $D$ should be the larger the larger FVF is.

From the data of Figure 4 we conclude that the temperature dependence of $D$ could be described by an Arrhenius law

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \tag{4}$$

where $Q$ is the activation energy of diffusion and $D_0$ is the prefactor. The values of prefactor and activation energy are higher for the diffusion in the conditioned sample than in the aged one (see Figure 4). Since both prefactor and activation energy for conditioned and aged samples differ only slightly, we concentrate our discussion on the differences in activation energy, because they influence diffusion rate exponentially. Our aim is to show that an increase in activation energy for the conditioned sample is sufficient for a quantitative description of data in Figure 4, and it could be reasoned through the corresponding changes in polymer morphology evaluated in section 3.

Which factors could be responsible for the change in activation energy? First of all, there are changes in the potential landscape of penetrant molecules due to polymer aging or conditioning. These changes in positions of local minima (energy of sorption sites) and width of their distribution are listed in Table 1 and presented schematically in Figure 5. (Note that in order to clarify Figure 5 we presented the saddle point positions as if they have the same energy.) In principle, aging could also alter saddle points energies $G^{\max}$ and $G^{\max}_{\mathrm{cond}}$ could become smaller than $G^{\max}_{\mathrm{aged}}$. However, the driving force responsible for these changes is expected to be weaker than the ones for local minima. This could be rationalized if we associate sorption sites and saddle points with less and more dense (or relaxed) regions of the polymer matrix, respectively. We assume these changes in $G^{\max}_{\mathrm{cond}}$ to be smaller than the ones introduced in the energetics of sorption sites (Figure 5). Furnished with this assumption, one can immediately relate the corresponding changes in sorption enthalpy and activation energy of gas diffusion:

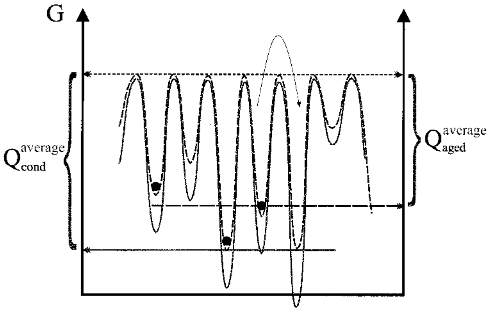

**Figure 5.** Illustration of potential landscape for small molecules in aged and conditioned polymer matrixes. Dashed lines correspond to aged while solid lines to conditioned samples. To simplify this illustration, the saddle point positions have the same energy.

$$-(H_{\mathrm{aged}} - H_{\mathrm{cond}}) = Q_{\mathrm{aged}} - Q_{\mathrm{cond}} \tag{5}$$

The minus before the difference of sorption enthalpies appears because they are defined with respect to the gas under standard conditions, while activated energies of diffusion are with respect to barrier height. The significance of eq 5 is that the entities on the left and on the right sides could be determined by experiments of different kinds. Namely, the change of enthalpy of sorption could be obtained from calorimetric measurements or calculated from the experimental sorption isotherms for conditioned and aged samples, while the value for activation energy of diffusion could be extracted from the data on sorption kinetics at different temperatures. To check the consistency of eq 5 with data on diffusion and parameters of SD model, indicated in the Table 1 and Figure 4, let us first note that $G^0_{\mathrm{aged}} - G^0_{\mathrm{cond}} = H^0_{\mathrm{aged}} - H^0_{\mathrm{cond}} - T(S^0_{\mathrm{aged}} - S^0_{\mathrm{cond}}) \approx H^0_{\mathrm{aged}} - H^0_{\mathrm{cond}}$. It is because the variations in the vibrational entropy of dissolved gas molecules induced by differences in $V^0_{\mathrm{h}}$ for aged and conditioned samples make a smaller effect on $G^0$ in comparison with that caused by change in elastic energy. Furthermore, a calorimetric experiment would give value of $H$ rather than of $H^0$, but as was shown in Appendix A, $H = H^0 - \sigma^2/4RT$ in the dilute regime. Since the values for activation energies of Figure 4 are also measured for the small concentration limit, one can rewrite (5) as

$$\begin{aligned} Q_{\mathrm{cond}} - Q_{\mathrm{aged}} &= (H^0_{\mathrm{aged}} - H^0_{\mathrm{cond}}) + \frac{1}{4RT}(\sigma^2_{\mathrm{cond}} - \\ &\sigma^2_{\mathrm{aged}}) \approx (G^0_{\mathrm{aged}} - G^0_{\mathrm{cond}}) + \frac{1}{4RT}(\sigma^2_{\mathrm{cond}} - \sigma^2_{\mathrm{aged}}) \end{aligned} \tag{6}$$

The substitution of the corresponding values from Table 1 in eq 6 gives the change in activation energy of diffusion 0.9 kJ/mol, which is in reasonable agreement with our data on sorption kinetics ($Q_{\mathrm{cond}} - Q_{\mathrm{aged}} = 1.1$ kJ/mol). The “morphological” reasons for the change in activation energy are the following: conditioning increases both the average site volume $V_h^0$ and the width in volume distribution $\sigma_V$ (Table 1). A larger site volume leads to a smaller elastic distortion (and energy) during sorption of gas molecule, and a broader distribution of free volumes offer more sites of low energy. Both of these factors are in favor of increasing $Q$ in the conditioned sample (Figure 5). Before proceeding with further discussion, we would like once again to note that the differences in parameters of SD model listed in Table 1 are rather small. That is why we do not want to overestimate the calculations based on eq 6 because they contain small differences of large values. What is significant is the difference in gas solubilities for aged and conditioned samples (Figure 1) as well as the corresponding changes in gas diffusivity (Figure 4). The fact that both of these two sets of experimental data of rather different origin could be described *quantitatively* by setting up similar changes of the order of 1 kJ/mol in the sorption enthalpies and the activation energies of diffusion we consider as a strong argument in favor of the assumptions underlying eq 5. The main point of interest for us is that the changes in the *elastic* part of sorption enthalpy evaluated within the SD model from sorption isotherms for aged and conditioned samples are about the same as the changes in activation energy of diffusion. This suggests that the changes in the elastic contribution to activation energy of diffusion are the main reason for the change of gas diffusivity due to polymer pretreatment. But before accepting this statement, one needs to consider another factor that could affect diffusivity, namely, the changes in relaxation dynamics of polymer chains.

The slight increase in the activation energy of $\gamma$-relaxation (Figure 2) in aged polymer is in favor of decreasing gas diffusivity, which is opposite to the experimental results of Figures 3 and 4. The $\beta$-process is strongly influenced by polymer pretreatment, but we do not expect that chain segments involved in the $\beta$-process are facilitating diffusion of molecules as small as $CO_2$ because of the following reasons: The activation energy of $CO_2$ is much smaller than that of the $\beta$-process, and therefore the time of residence for gas molecules $\tau_{gas}$ is also much smaller than the characteristic time of $\beta$-relaxation $\tau_\beta$. To estimate these times, let us assume that they could be described by an Arrhenius law $\tau = \tau_0 \exp(Q/RT)$, where $2\pi/\tau_0$ is attempt frequency and $Q$ is an activation energy of the corresponding process. The condition for maximum in relaxation spectra could be written as $2\pi f\tau = 1$, where $f$ is the pendulum's frequency ($f = 0.73$ Hz). Taking the reasonable value for $\tau_0 \approx 10^{-13}$ s and the measured temperature of $\beta$-peak $T_\beta = 360$ K, one can estimate $Q_\beta = RT_\beta \ln(\tau/\tau_0) \approx -RT_\beta \ln(2\pi f\tau_0) \approx 94$ kJ/mol, which is in good agreement with the literature data 90−110 kJ/mol.[18] Then, $\tau_\beta/\tau_{gas} = \exp[(Q_\beta - Q_{gas})/RT \approx 10^{10}$. We conclude that observed modifications in chain dynamics caused by polymer pretreatment (Figure 2) are not strong enough for being responsible for the corresponding changes in diffusivity (Figures 3 and 4).

Therefore, we infer that the observed changes in $CO_2$ and Ar transport for aged and conditioned samples of BPA-PC are mainly due to a modification of elastic contribution to the activation energy. A stronger distortion of the polymer matrix during dissolution of molecules leads to a higher value for elastic energy and, therefore, to a lower activation energy of diffusion. This explains why transport is quicker in aged than in conditioned samples. Certainly, the next question arising is about the limits of applicability of our elastic arguments. The answer is linked to the relative sizes of gas molecules and sorption sites.

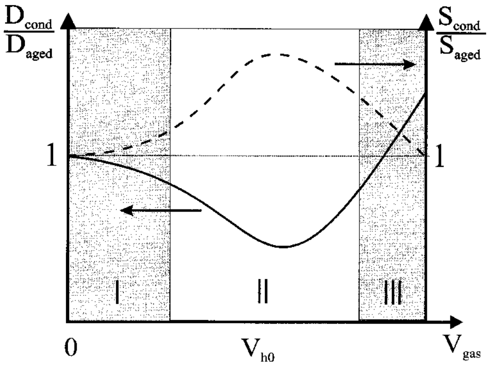

**Figure 6.** Ratios of diffusion coefficients and solubilities for conditioned and aged polymer samples as a function of molecular volume of gas. The solid line describes changes in diffusivity (left axes) while the dashed line illustrates modifications in solubility $S$ (right axes).

## 5. Effect of Solute Size

In this section we discuss how the effect of aging/conditioning on the gas diffusion depends on the relative difference of penetrante and hole sizes. In addition, we also consider the corresponding changes in gas solubility, because of the close relation between changes in sorption and transport behavior of small molecules caused by polymer pretreatment. In principle, the following three regimes are possible:

*(I) Gas Molecules Being Smaller Than the Size of Occupied Holes* ($V_g < V_h$). In this situation there is no elastic contribution to sorption enthalpy, i.e., $H_{el} = 0$. Therefore, there are no changes in sorption enthalpy during aging and solubility of small molecules in this regime which is not modified by polymer pretreatment (Figure 6). Indirect support for this conjecture can be found in the observation that despite the distribution of the hole sizes in glassy polymer, the sorption isotherms of small molecules such as He or water can be described using a single value for the sorption enthalpy (ref 8). Certainly, this consideration could fail if penetrant molecules form clusters or solvation effects are present. Similarly, one can speculate that the diffusivities of penetrants, which are smaller than the typical size of occupied sorption sites, are not expected to be influenced by aging or conditioning (region I in Figure 6). These conclusions could be supported by literature data. Akele et al.[16] report that, within experimental errors, they did not observe an influence of aging on the water diffusion and sorption in BPA-PC. Jordan and Koros[20] state that rather heavy conditioning had no significant influence on helium permeability in various polycarbonate materials, which also agrees with our consideration.

*(II) Gas Molecules Having about the Size of Occupied Holes* ($V_g \geq V_h$). In this case elastic distortion of the polymer matrix during dissolution arises. The elastic energy due to this distortion increases with free volume relaxation, which has the corresponding effect on diffusivity (region II of Figure 6), as it was discussed in detail in section 4. Concerning gas sorption, in the elastic regime the elastic part of sorption enthalpy increases with decreasing free volume and the solubility is lowered. According to eq 5, in this regime the effect

of polymer aging or conditioning on the enthalpy of gas sorption is just opposite to that on the activation energy of diffusion.

*(III) Gas Molecules Which Are Considerably Larger Than the Typical Void Size ($V_g \gg V_h$).* Incorporation of these molecules induces viscoelastic flow of the polymer, and one could not expect elastic arguments of section 4 to be valid. A higher number of polymer segments are involved in transport of larger molecules, and the available free volume that is needed to assist these collective motions becomes a dominant factor that controls diffusion. Therefore, diffusion rates in this regime go down as the free volume decreases, in agreement with predictions of FV theory[3] and experimental results of refs 4 and 5. For an instructive illustration of "interstitial" and "free volume dominant" cases one can reconsider Figure 2 of this work. Although that there are difference between diffusive jumps of solute molecules and movements of structural units responsible for $\beta$- and $\gamma$-relaxation of the polymer matrix, one can note the following: The dynamics of smaller structural units involved in the $\gamma$-process is practically unaffected by aging ("interstitial"-type regime). On the other hand, movements of larger structural units participating in the $\beta$-process are totally suppressed in the aged sample as result of decreasing free volume ("free volume controlled regime"). This last regime is represented as region III of Figure 6. Certainly, collection of additional experimental data on diffusion of penetrants of different sizes in the same aged-conditioned couple is desirable, to reconstruct Figure 6 more accurately.

It is also interesting to compare the intuitive arguments mentioned above about the difference in mechanisms of diffusion for smaller and larger penetrants with information obtained from computer simulations. As was seen in numerous simulations, diffusion of smaller penetrant in glassy structures could be visualized as a sequence of infrequent jumps between more or less permanent "cavities" or sorption sites in polymers (ref 25). For diffusion of bigger molecules these preexisting holes are too small to adopt penetrant molecules. To perform diffusive step in this situation, a diffusant has to build itself some space around (ref 26). For a real (not simulated) polymer−gas system it could be difficult to detect a crossover between these two regimes. Our discussion suggests the possibility to locate this crossover through the measurements of change in transport rates of penetrant due to modifications of polymer free volume.

Another somehow surprising conclusion could be drawn about gas sorption for regime III. Since the excess strain needed to accommodate solute molecule in a void is created by plastic rather than by elastic deformation, the elastic part of sorption enthalpy practically does not depend on free volume relaxation. To show this, let us estimate how the equilibrium concentration of dissolved gas molecules changes with their size. According to eq 2 the enthalpy of sorption consists of elastic and rest parts. The rest part is assumed to be independent of the pretreatment of polymer and could be evaluated using, for example, the Flory−Huggins parameters for the given polymer−solvent couple. The elastic contribution $H_{el}$ could be estimated within the simplified assumption that the gas molecules and holes are spherical. According to the continuum elasticity calculations of Eshelby,[17] for a sphere of volume $V_g$ placed in the hole of volume $V_h \le V_g$ the elastic energy contribution equals

$$G_{el}(V_h) = \frac{2\mu}{3\gamma}\frac{(V_g - V_h)^2}{V_h} \qquad (7)$$

where $\mu$ is the shear modulus of polymer glass and the dimensionless factor $\gamma = (1 + 4\mu/3\kappa)$ depends on the bulk modulus $\kappa$ of the elastic sphere. For $\kappa$ being the same as the bulk modulus of the matrix and Poisson's ratio $\nu = {}^1/_3$, we obtain $\gamma = 1.5$. (Note that in the original work of ref 13 $\gamma$ did not appear in estimations of elastic energy, because there it was assumed that a gas molecule is stiff, i.e., $\kappa \to \infty$ and $\gamma \to 1$. However, in the following publications of our group[10,11] it was supposed that the small molecules have a similar bulk modulus compared to that of the polymer. This may be justified by comparing bulk moduli of liquids composed of small molecules which are about 1 GPa with those of glassy polymers being about 3 GPa.) Let us note at the moment that neither $CO_2$ molecules nor sorption sites are spherical and that application of continuum elasticity theory (eq 7) for estimations on the molecular length scales could be also questioned. However, this model could be sufficient for our consideration. For the elastic regime (region II of Figure 6) one can write

$$c \propto \exp\left(-\frac{2\mu}{3\gamma RT}V_h\left(\frac{V_g}{V_h} - 1\right)^2 - \frac{H_r}{RT}\right) \qquad (8a)$$

so that the values of both volumes of gas molecule and void influence the gas solubility. Note that a more accurate expression for concentration, which takes into account a distribution of void volumes, is provided by the SD model. This distribution influences strongly solubility of molecules of "intermediate" size in polymer, but it, as we will see in a moment, plays no role in consideration of solubility for larger molecules. How should one change eq 8a in order to describe the sorption of larger molecules? Let us assume that the polymer matrix starts to respond nonelastically when the ratio of the solute molecule to the void volumes reaches the value $V_g/V_h = 1 + \alpha$, where $\alpha$ is a material constant. We need to estimate the elastic energy for the equilibrium situation when a big molecule of volume $V_g$ is already adopted in the hole of volume $V_h$. If the initial hole size was smaller than $V_h^{\otimes} = V_g/(1 + \alpha)$, then some viscoelastic relaxation of excess stress occurs in polymer. Substitution of this value of critical hole size in eq 6a gives us the estimation of equilibrium solute concentration in viscoelastic regime (region III of Figure 6):

$$c^{\otimes} \propto \exp\left(-\frac{2\mu}{3\gamma RT}\frac{\alpha^2}{1 + \alpha}V_g - \frac{H_r}{RT}\right) \qquad (8b)$$

Note that there is no dependence on hole volume $V_h$ in eq 8b. Particularly, this means that equilibrium concentration could be described with the single value of sorption enthalpy (no energy distribution) and that for big enough solute molecules aging does not affect equilibrium solubility, as indicated in Figure 6. Certainly, some care should be exercised in applications of eq 8b because of possible plastification of the glassy matrix. In this case the polymer shear modulus $\mu = \mu(c)$ depends on concentration and decreases dramatically in the vicinity of the glass transition. The conclusion about the independence of equilibrium concentration of big molecules on the initial parameters of volume distribution could be also expressed in a different way within the framework of SD model. Namely, the width of sorption energy distribution becomes zero for small enough and for big enough molecules, and the distribution of sorption energies plays a role for solutes of sizes about $V_h^0 - \sigma_V < V_g < V_h^0 + \sigma_V$ only. This seems to be in agreement with data on diffusion of different gases in BPA-PC,[7] but again more experimental points are needed in order to model this behavior quantitatively.

Before finishing this section, let us note that a transition between different regimes for gas sorption and diffusion discussed here could be achieved not only by variations of solute size but also through a change in solute concentration. For example, the $CO_2$–BPA-PC system at small gas concentrations belongs to regime II. Gas molecules occupy first bigger holes or, in different words, sites with more negative sorption enthalpy. While increasing a gas concentration, sites of smaller and smaller volume have to be occupied, and at high enough concentrations one could expect a transition to regime III. The possibility of this transition gives an alternative explanation for results of ref 9, discussed in the Introduction.

## 6. Conclusions

It is customary to relate transport of small molecules in amorphous materials to the frozen in “free volume”. The corollary of such consideration is that the diffusion is faster in more “open” matrices having a higher free volume. We discuss in this work a different situation where the opposite is true. In our experiments on diffusion of $CO_2$ and Ar in BPA-PC (as well as in experiments of refs 8 and 9) the small increase in polymer free volume due to conditioning resulted in deeper traps for penetrant molecules that gives rise to slowing down of gas diffusion. We argued that the difference in gas diffusion in aged and conditioned samples could be described through the difference in corresponding activation energies. The later could be correlated with the changes in enthalpy of sorption which stems from the polymer pretreatment. We would like to stress that though the reported effects of aging and conditioning on gas transport are relatively small, they are important as an additional examination of our understanding of diffusion in glasses. Transport of $CO_2$ and Ar in BPA-PC falls in the regime where diffusive jump is not assisted by cooperative motion of many polymer segments, which takes place during diffusion of bigger molecules, and the elastic energy due to occupation of sorption sites by gas molecules reduces the activation energy of diffusion. This elastic factor is not included in either FV[3] or molecular level[19] theories of gas diffusion but, as suggested by our work, could be an important ingredient of a transport mechanism of small molecules in glasses.

**Acknowledgment.** We thank J. Bohlen and M. Guerdane for interesting discussions. We are grateful for financial support provided by the Deutsche Forschungsgemeinschaft.

## Appendix A

As was shown in ref 13, the Gaussian energy distribution of eq 3 together with Fermi–Dirac’s statistics for the occupancy of sorption sites leads to the following expression for the $c-p$ isotherm:

$$c \propto \int_{-\infty}^{+\infty} \frac{\exp[-(G - G^0)^2/\sigma^2]}{1 + p^{-1}\exp(G/RT)}\, dG \qquad (A1)$$

This integral could be evaluated in the small pressures limit $p \to 0$ as

$$c \propto p \exp\left[-\frac{1}{RT}\left(G^0 - \frac{\sigma^2}{4RT}\right)\right] \propto p \exp\left[-\frac{1}{RT}\left(H^0 - \frac{\sigma^2}{4RT}\right)\right] \qquad (A2)$$

Now there are two possibilities to calculate the heat of sorption. First, using standard definition of heat of sorption together with eq A2, one can get

$$H = -\frac{\partial \ln c}{\partial(1/RT)} = H^0 - \frac{\sigma^2}{2RT} \qquad (A3)$$

Another way is to define *apparent* heat of sorption, using the formal similarity of eq A2 with the van’t Hoff relationship as

$$H = H^0 - \frac{\sigma^2}{4RT} \qquad (A4)$$

Expression A4 corresponds to the usual procedure for evaluation of heat of sorption from a series of sorption isotherms, measured for different temperatures within the assumption that $H(T)$ = const in a corresponding temperature interval. A similar ambiguity exists for the definition of activation energy of diffusion $Q$, when the latter depends on the temperature. Using a standard definition of $Q$ together with Gaussian distribution of site energies, one can get (ref 24)

$$Q = -\frac{\partial \ln D}{\partial(1/RT)} = Q^0 + \frac{\sigma^2}{2RT} \qquad (A5)$$

while the activation energy, determined by a linear fit for experimental data, plotted in Arrhenius coordinates ($\ln D$ vs $1/T$) would be given by

$$Q = Q^0 + \frac{\sigma^2}{4RT} \qquad (A6)$$

In this work we are using definitions (A4) and (A6), because they correspond to our experimental procedures.

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MA990642A